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# Application of GC/ITD (Gas Chromatography/Ion Trap Detector) to Environmental Analysis (Journal Version)

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16. ABSTRACT

The utility of gas chromatography for environmental analysis has been demonstrated and remains the basis for many regulatory organic methods. The choice of detectors has expanded rapidly and now encompasses a full range of viable detectors. The necessity for mass spectrometric characterization of gas chromatographic effluents stems from the complexity of the matrices associated with environmental chemistry. There are currently several mass spectrometer types being used in conjunction with the gas chromatograph. These include magnetic sector analyzers, quadrupole analyzers, time of flight analyzers, and ion storage devices such as quadrupole ion trap and ion cyclotron resonance (ICR) mass spectrometers. This paper is concerned with the latter, the application of the ion trap mass spectrometer to environmental analysis. Environmental analysis using the ITD has generally proceeded along two lines: first the application of the ITD to volatile and semi-volatile analytes, and second, the evaluation of ITD technology for inclusion into the U.S. EPA analysis program. The GC/ITD has provided representative mass spectra for the analysis of purge-and-trap volatiles and hazardous waste steam distillate. The ability to obtain library matchable EI spectra on a routine basis indicated that the ITD technique can successfully analyze environmental samples.

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# Application of GC/ITD to Environmental Analysis

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The utility of gas chromatography for environmental analysis has been demonstrated (1) and remains the basis for many regulatory organic methods (2). The choice of detectors has expanded rapidly and now encompasses a full range of viable detectors. Examples of detectors used in the determination of GC effluents include simple thermoconductivity, electron capture, photoionization, Hall, and a recent addition, the mass spectrometer.

The necessity for mass spectrometric characterization of gas chromatographic effluents stems from the complexity of the matrices associated with environmental chemistry. The time-intensity information associated with gas chromatography alone has proven insufficient to effectively characterize such complex matrices. The mass spectrum adds new vectors with the maximum specificity being derived from the electron ionization (EI) mass spectrum, which contains a number of fragment ions. Specificity to a lesser degree is gained through the use of other ionization techniques such as chemical ionization (CI).

There are currently several mass spectrometer types being used in conjunction with the gas chromatograph. These include magnetic sector analyzers, quadrupole analyzers, time of flight analyzers, and ion storage devices such as quadrupole ion trap and ion cyclotron resonance (ICR) mass spectrometers. This paper is concerned with the latter, the application of the ion trap mass spectrometer to environmental analysis. Earlier versions of ion trap mass spectrometers as reviewed by Todd et al. (3) have undergone marked improvement, both in mechanics and mode of mass analysis. These improvements, including RF-only scanning and helium damping gas (4), led to the production of the first commercial ion trap mass spectrometer by Finnigan MAT. This instrument, called the Ion Trap Detector™ (ITD™) is characterized by a trapping cell consisting of two hyperbolic end cap electrodes and a single hyperbolic (solid of revolution) central electrode. The electron beam is gated to produce discrete packets of electrons. Ionization occurs through electron ionization. The molecular ions and associated fragment ions are trapped by a cyclotron RF voltage applied to the central electrode. Low trapping RF voltages result in all ions being trapped. Ion ejection occurs via sweeping the trapping RF voltage. Instability is produced in the cyclotron orbit, causing ion ejection. Detection of the ejected ions occurs at the electron multiplier located behind the aperture at the center of one end cap.

The operating characteristics of the ITD require a very modest vacuum. Increasing the pressure at a constant ion residence time will produce spectra that are inconsistent with electron ionization phenomena due to ion-molecule reactions. This can be best described in the following manner. As the mass spectrum is swept (RF voltage sweep), the residence time for the ions in the cell will vary depending upon their mass. Those ions with the largest residence time in the trap will have a higher probability of undergoing ion-molecule reactions. This anomalous behavior has been overcome using segmented scans under computer control and has resulted in the recording of electron ionization mass spectra suitable for library matching. It is not the purpose of this paper to explain the theory of ITD methodology, but the above gives a general overview of the ITD concept.

Environmental analysis using the ITD has generally proceeded along two lines: first the application of the ITD to volatile and semivolatile analytes, and second, the evaluation of ITD technology for inclusion into the U.S. EPA analysis program. The Federal and regulated community is concerned with the determination of organic analytes that have associated human health or ecological risk. The priority pollutant list contains 129 organic chemicals described as volatile and semivolatile acid/base/neutral extractables.

The methodologies associated with the analysis of this class of compounds are described in the U.S. EPA's 600 series methods (5) and in the protocols used in the Superfund Contract Laboratory Program (CLP) (6). Method 625 describes the GC/MS analysis of the priority pollutants that are extractable. Method 624 describes the purge-and-



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**Table 1.**
**DFTPP Tuning Criteria**

| *m/z* | Recommendation | 1975 Criteria |
|---|---|---|
| 51 | 15–75% of *m/z* 198 | 30–60% of 198 |
| 127 | 15–60% of *m/z* 198 | 40–60% of 198 |
| 275 | 10–60% of *m/z* 198 | 10–30% of 198 |
| 198 or 442 | base peak | 198 must be base; 442 > 40% of 198 |
| 68 | ≤ 2% of *m/z* 69 | < 2% of 69 |
| 70 | ≤ 2% of *m/z* 69 | < 2% of 69 |
| 197 | ≤ 1% of *m/z* 198 | < 1% of 198 |
| 199 | 4.5–9% of *m/z* 198 | 5–9% of 198 |
| 443 | 15–24% of *m/z* 442 | 17–23% of 442 |
| 442 | ≥ 40% of m/z 198 if 198 is base peak | |
| 198 | ≥ 30% of m/z 442 if 442 is base peak | |
| 365 | ≥ 0.5% of *m/z* 198 | > 1% of 198 |
| 441 | delete criterion | present, < 443 |

trap GC/MS of volatiles and semivolatiles. The Superfund CLP program has developed methodologies that are similar to the 600 methods except extended to a wider variety of matrices.

The application of ITD technology to the methods listed above must meet several requirements regarding quality control. In order to create data of known quality, the Agency has determined that mass spectrometers must meet tuning criteria (7). Also, the stability of the instruments must be controlled in order to meet response-factor (8) criteria. Investigation of these two criteria (9, 10) has led to conclusions that the spectral behavior of the ion trap is similar to magnetic sector mass spectrometers and does not suffer from the mass discrimination sometimes ascribed to quadrupole mass analyzers. Table 1 lists the instrument relative abundance criteria attained by a number of mass spectrometers in a round-robin study of tuning criteria (10). As a result of this new tuning study, the EPA is reevaluating its tuning criteria. It is expected that revised tuning criteria will be adopted (10) that will encompass all mass spectrometer designs.

## Tuning Criteria

The use of DFTPP as a benchmark tuning compound was developed by Budde et al. (7) and has been used as a quality control parameter by the U.S. EPA and adopted by other Federal and State Agencies for their quality control program. This benchmark has provided a great wealth of data from which comparisons can be derived. The spectrum of DFTPP using the ITD is shown in Figure 1 along with the corresponding quadrupole and magnetic sector spectra. It is interesting to note the apparent agreement between the spectrum from the ITD and the other spectra.

## Quantitation

GC/MS provides a mechanism to quantitate compounds in environmental samples because of the excellent gas chromatographic separation (especially when fused silica capillary columns are used) and the selectivity of the mass spectrometer. Typically a selected ion is used rather than the total ion signal, resulting in greater sensitivity. For the reasons of specificity and sensitivity, GC/MS is the preferred quantitative method. GC/ITD also provides quantitative results.

## Experimental

All analyses were performed on a Finnigan MAT Model 705 ITD consisting of an IBM® PC/XT with version 3.00 software. Purge-and-trap analysis of volatiles was done on a Tekmar Dynamic Headspace Concentrator with a 25-ml frit sparger. A J&W 30 m × 0.32 mm DB-624 capillary column was connected directly to the heated purge line. The column exit was connected to the ITD heated transfer line installed in the GC oven wall. All other conditions were per EPA method 624 (5).

The hazardous waste sample was a steam distillate of a soil sample obtained from a hazardous waste site. A methylene chloride solution was chromatographed on a Restek 30 m × 0.25 mm RLX-5 capillary column. A Perkin-Elmer Sigma 2000 gas chromatograph was used and was equipped with an autosampler and splitless injector.

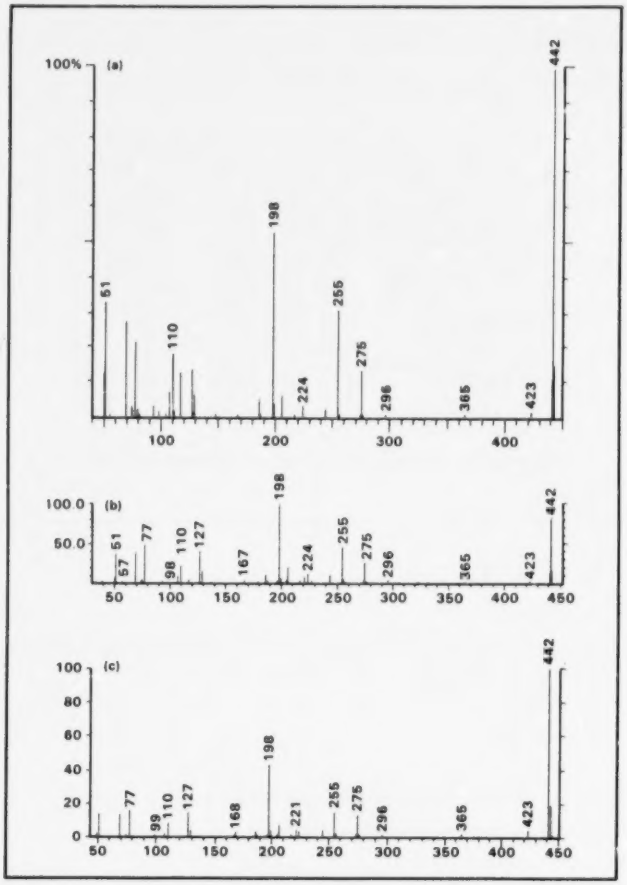


**Figure 1.** Comparison of DFTPP spectra (a: ITD, b: quadrupole, c: magnetic sector)

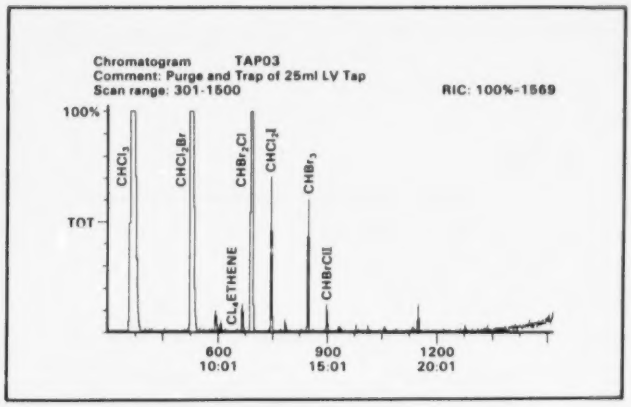


**Figure 2.** GC/ITD reconstructed ion chromatogram (RIC) of drinking water supply

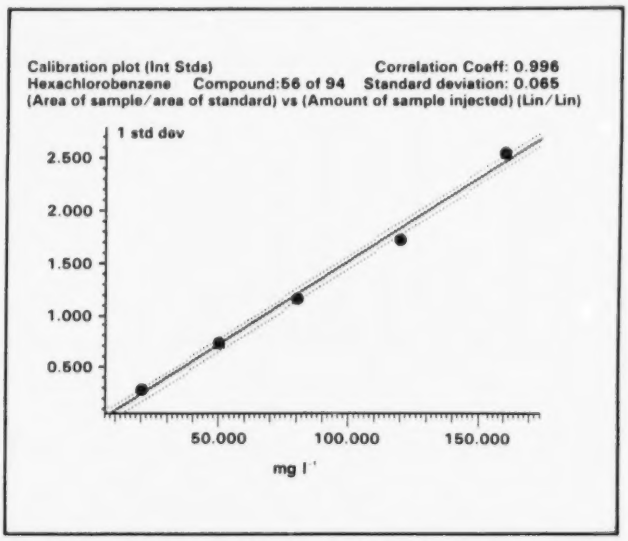


**Figure 3.** Typical response curve—hexachlorobenzene

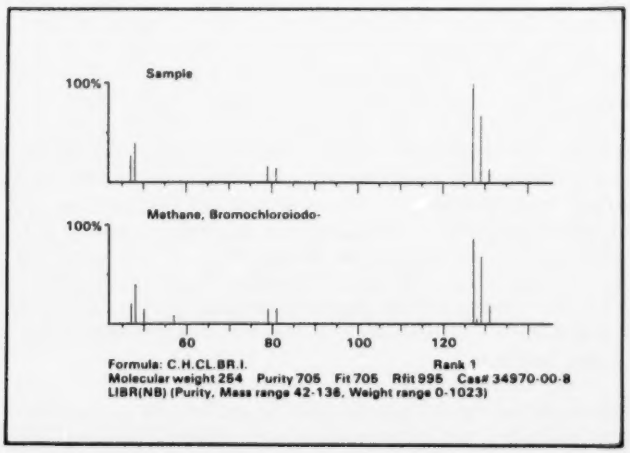


**Figure 4.** Spectrum of tentatively identified volatiles in the drinking water supply

## Results

Figure 2 shows a GC/ITD analysis of a 25 ml drinking water sample using purge-and-trap concentration. Chloroform, bromodichloromethane, and dibromochloromethane were identified. These analytes are commonly found in drinking water supplies and are the result of halogenation of the domestic supply prior to distribution. However, three other trihalomethanes were also identified at levels that are as much as 1 000 times lower than chloroform. These compounds are bromoform and two trihalomethanes that contain iodine, (dichloroiodomethane and chlorobromoiodomethane). The two latter compounds have been identified previously but not with purge-and-trap concentration. Also present in trace amounts were tetrachloroethene, toluene, and ethylbenzene. The data show the sensitivity and dynamic range of purge-and-trap analysis coupled with ion trap detection. Note the excellent signal-to-noise ratio of the analysis, indicative of a robust analytical technique.

A typical response curve is shown in Figure 3 for hexachlorobenzene. The linearity is approximately plus or minus one standard deviation over the analytical range.

The ability to library-match (search) spectra obtained from sample analysis is important for environmental

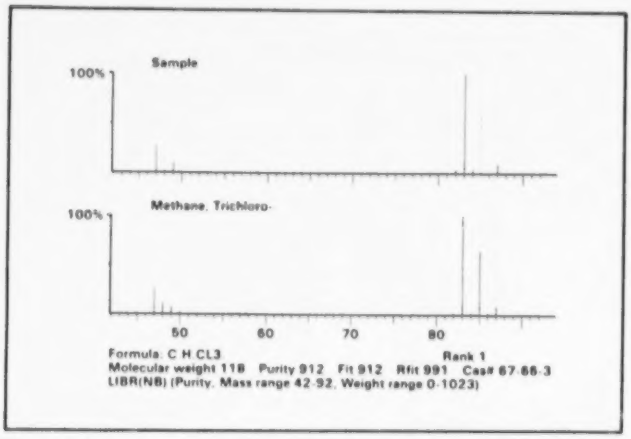


**Figure 5.** Spectrum of tentatively identified volatiles in the drinking water supply

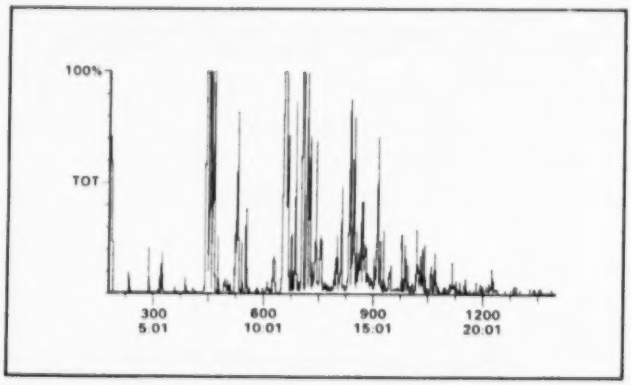


**Figure 6.** Chromatogram of representative hazardous waste

analysis. Figures 4 and 5 show the identification of the volatile compounds found in the drinking water supply.

The analysis of the combined volatile-semivolatile fraction of a representative hazardous waste sample obtained by steam distillation can be seen in Figure 6. Table 2 gives the compounds quantitated by internal standardization using ITD software. Although there are many other compounds shown in Figure 6 that were not quantitated, the data in Table 2 represent compounds for which no standards were available and, therefore, compounds that could not be unambiguously identified solely from the library matched spectra. The percentage of library matched, tentatively identified compounds is what would be expected in general as reported by Shackleford et al. (11). Representative mass spectra along with the corresponding library spectra are given in Figures 7 and 8 for the largest peak in the chromatogram and one of the smallest.

In conclusion, the GC/ITD has provided representative mass spectra for the analysis of purge-and-trap volatiles and hazardous waste steam distillate. The ability to obtain library matchable EI spectra on a routine basis indicated that the ITD technique can successfully analyze environmental samples.

**Table 2. Quantitation Report for Hazardous Waste Sample**

| Cal | Name of Compound | S | Scan# | R Time | Calc Amt(A) | Units |
|---|---|---|---|---|---|---|
| 7 | d14 1,4DICIBENZ(Istd) | I | 517 | 8:30 | 40.000 | ng/ul |
| 25 | d-8 NAPHTHALENE(Istd) | I | 716 | 11:57 | 40.000 | ng/ul |
| 40 | d-10ACENAPHTHENE(Istd) | I | 985 | 16:26 | 40.000 | ng/ul |
| 60 | d-10PHENANTHRENE(Istd) | I | 1209 | 20:09 | 40.000 | ng/ul |
| 83 | d-12 CHRYSENE(Istd) | I | 1616 | 26:57 | 40.000 | ng/ul |
| 6 | 1,3 DICHLOROBENZENE | A | 512 | 8:33 | 0.840 | ng/ul |
| 8 | 1,4 DICHLOROBENZENE | A | 520 | 8:41 | 116.757 | ng/ul |
| 9 | 1,2 DICHLOROBENZENE | A | 548 | 9:09 | 150.550 | ng/ul |
| 10 | BENZYL ALCOHOL | A | 551 | 9:12 | 10.930 | ng/ul |
| 13 | HEXACHLOROETHANE | A | 593 | 9:54 | 7.744 | ng/ul |
| 23 | BENZOIC ACID | A | 720 | 12:09 | 498.283 | ng/ul |
| 24 | 1,2,4 TRICHLOROBENZENE | A | 712 | 11:53 | 609.685 | ng/ul |
| 26 | NAPHTHALENE | A | 718 | 11:59 | 13.029 | ng/ul |
| 28 | HEXACHLOROBUTADIENE | A | 748 | 12:29 | 73.039 | ng/ul |
| 35 | 2-CHLORONAPHTHALENE | A | 905 | 15:06 | 79.506 | ng/ul |
| 56 | HEXACHLOROBENZENE | A | 1162 | 19:23 | 3.514 | ng/ul |

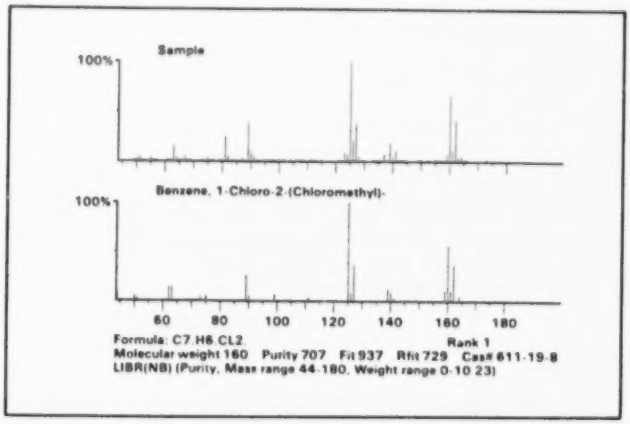


**Figure 7.** Selected spectrum derived from hazardous waste analysis; from the largest peak in the chromatogram

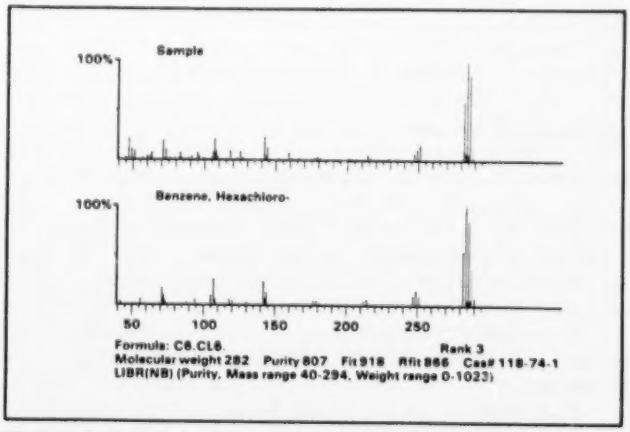


**Figure 8.** Selected spectrum derived for hazardous waste analysis; from one of the smallest peaks in the chromatogram

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## Biographies

**Steven M. Pyle** has a B.S. degree in Chemistry from the University of Cincinnati and a M.S. degree in Chemistry from Xavier University in Ohio. From 1976 to 1980, he was a chemist in the Health Effects Research Laboratory at the United States Environmental Protection Agency in Cincinnati developing DNA damage assays. In 1981, he joined the Environmental Monitoring and Support Laboratory (EMSL) of the U.S. EPA in Cincinnati to do GC/MS analysis. Presently, he is located at the EMSL-Las Vegas laboratory developing methods for advanced instrumentation. Besides the field of GC/MS, his present interests include Supercritical Fluid Chromatography and Fourier Transform Infrared Spectroscopy.

**Ronald K. Mitchum** has a B.S. degree in Chemistry from Southwestern Oklahama State University and holds a Ph.D. in Physical Organic Chemistry from Oklahoma State University. After postdoctoral appointments at Universities of Houston; Warwick, England; and Nebraska, he was selected as a staff research chemist at the National Center for Toxicological Research (NCTR) where he continued the investigation of the fundamentals of mass spectrometry and established himself in the areas of biomedical and environmental mass spectrometry. As Director of the Chemistry Division at the NCTR, he was responsible for many areas of analytical chemistry including NMR, mass spectrometry, classical spectroscopies, and the chemistries associated with the analysis of carcinogens and biopolymers. Presently, Dr. Mitchum is the Director of the EPA's Quality Assurance and Methods Development Division located in the Environmental Monitoring Systems Laboratory in Las Vegas, Nevada, where he is responsible for a broad range of environmental programs.

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